

A propensity for *n*- ω -amino acids in thermally altered Antarctic meteorites

Aaron S. BURTON^{1,2*}, Jamie E. ELSILA¹, Michael P. CALLAHAN¹, Mildred G. MARTIN^{1,3},
Daniel P. GLAVIN¹, Natasha M. JOHNSON¹, and Jason P. DWORKIN¹

¹NASA Goddard Space Flight Center and the Goddard Center for Astrobiology, Greenbelt, Maryland 20771, USA

²NASA Postdoctoral Program Administered by Oak Ridge Associated Universities, Oak Ridge, Tennessee 37831, USA

³Catholic University of America, Washington, District of Columbia, USA

*Corresponding author. E-mail: aaron.s.burton@nasa.gov

(Received 01 November 2011; revision accepted 04 February 2012)

Abstract—Asteroids and their fragments have impacted the Earth for the last 4.5 Gyr. Carbonaceous meteorites are known to contain a wealth of indigenous organic molecules, including amino acids, which suggests that these meteorites could have been an important source of prebiotic organic material during the origins of life on Earth and possibly elsewhere. We report the detection of extraterrestrial amino acids in thermally altered type 3 CV and CO carbonaceous chondrites and ureilites recovered from Antarctica. The amino acid concentrations of the thirteen Antarctic meteorites ranged from 300 to 3200 parts-per-billion (ppb), generally much less abundant than in amino acid-rich CI, CM, and CR carbonaceous chondrites that experienced much lower temperature aqueous alteration on their parent bodies. In contrast to low-temperature aqueously altered meteorites that show complete structural diversity in amino acids formed predominantly by Strecker–cyanohydrin synthesis, the thermally altered meteorites studied here are dominated by small, straight-chain, amine terminal (*n*- ω -amino) amino acids that are not consistent with Strecker formation. The carbon isotopic ratios of two extraterrestrial *n*- ω -amino acids measured in one of the CV chondrites ($\delta^{13}\text{C}$ approximately -25‰) are consistent with ^{13}C -depletions observed previously in hydrocarbons produced by Fischer-Tropsch type reactions. The predominance of *n*- ω -amino acid isomers in thermally altered meteorites hints at cosmochemical mechanisms for the preferential formation and preservation of a small subset of the possible amino acids.

INTRODUCTION

The delivery of organic compounds by meteorites to the early Earth and other planetary bodies could have been an important source of prebiotic material required for the emergence of life (Dodd 1981; Chyba and Sagan 1992; Sephton 2002). The diversity and abundance of indigenous organic compounds vary significantly among carbonaceous chondrites, depending on their mineralogy and alteration histories (Kvenvolden et al. 1970; Cooper et al. 2001; Sephton 2002; Glavin et al. 2010a). Amino acids of extraterrestrial origin have been reported previously in just three of the eight carbonaceous chondrite groups (see Glavin et al. 2010a and references therein). These amino acid-containing CI, CM, and CR carbonaceous chondrite groups all show evidence of relatively low-temperature parent-body aqueous alteration, and contain up to 22% water by weight (Weisberg et al. 2006). Other

carbonaceous chondrites have also experienced some aqueous alteration (e.g., CV and CO), but typically have less than 3% water and have instead been more influenced by thermal alteration at temperatures of up to 900 °C or higher (reviewed in Krot et al. [2006] and Huss et al. [2006]). Previous analyses of the thermally altered CV3 carbonaceous chondrites Allende and Mokoia found them to be essentially devoid of amino acids (Cronin and Moore 1971, 1976), whereas at least one fragment of Allende was reported to contain significant amounts of terrestrial L-amino acid contamination (Botta et al. 2002). However, recent analyses of the Almahata Sitta polymict ureilite that experienced temperatures of 1200–1300 °C on the parent asteroid showed that this meteorite contains trace, but quantifiable levels of extraterrestrial amino acids (Glavin et al. 2010b; Herrin et al. 2010; Zolensky et al. 2010; Burton et al. 2011). This finding raised the possibility that other thermally altered meteorites, including CV and CO

carbonaceous chondrites and additional ureilites, also contain extraterrestrial amino acids.

Recently, we demonstrated a correlation between parent-body processing and amino acid abundances and distributions among the aqueously altered CM, CI, and CR meteorites (Glavin et al. 2010a). To determine if there is a similar correlation between amino acid abundances and thermal alteration, we have expanded our investigation of amino acids in meteorites to include a reasonable sampling of thermally altered meteorites: five CV3 carbonaceous chondrites, three CO3 carbonaceous chondrites, and five ureilites recovered from Antarctica, as well as a fragment of Allende (a CV3 chondrite recovered in Mexico; King et al. 1969). Ureilites are believed to represent the mantle material of a partially melted, carbon-rich asteroid (Mittlefehldt et al. 1998; Goodrich et al. 2004), possibly derived from impact shock heating or partial melting of CV chondrite-like material (Higuchi et al. 1976; Rubin 1988; Goodrich 1999). The CO carbonaceous chondrites have been placed in the same clan as the CMs, but have been more strongly influenced by thermal alteration and have petrologic characteristics in common with CV carbonaceous chondrites (Weisberg et al. 2006). Amino acid analyses of meteorite extracts were performed by ultra high-performance liquid chromatography with UV-fluorescence detection and time-of-flight mass spectrometry (LC-FD/ToF-MS). For comparison with the Antarctic meteorites, we also measured the amino acid composition of a sample of Antarctic blue ice collected from the Graves Nunatak region underneath one of the CV3 carbonaceous chondrites studied here (GRA 06101). To our knowledge, we report the first conclusive evidence for extraterrestrial amino acids in CV3 and CO3 carbonaceous chondrites and Antarctic ureilites. With the exception of Allende, none of the meteorites studied here have been previously analyzed for amino acids.

MATERIALS AND METHODS

Antarctic Meteorites

Samples were allocated to us by the ANSMET Meteorite Working Group and are listed, along with parent number, sample split, and the mass we extracted for this study. The ureilites were: Allan Hills A77257 (ALHA77257, [145, 37]; 96.3 mg), Elephant Moraine 83309 (EET 83309, [56, 0]; 433 mg; polymict), Lewis Cliffs 85328 (LEW 85328 [53, 43]; 416 mg), Graves Nunataks 95205 (GRA 95205, [35, 28]; 403 mg), Larkman Nunataks (LAR 04315 [49, 3]; 398 mg; anomalous); the CV3 carbonaceous chondrites were: Allan Hills 84028 (ALH 84028; [131, 29]; 400. mg), Elephant Moraine 96026 (EET 96026 [49, 45]; 434 mg), La Paz Icefield 02206 (LAP 02206 [29, 2]; 435 mg), Graves

Nunataks 06101 (GRA 06101; 184.4 mg), Larkman Nunataks 06317 (LAR 06317 [7, 3]; 444 mg); the CO3 carbonaceous chondrites were: Allan Hills A77307 (ALHA77307 [134, 56]; 389 mg), Miller Cliffs 05013 (MIL 05013 [10, 3]; 576.8 mg), and Dominion Range 08006 (DOM 08006 [17, 9]; 425 mg). Crushed serpentine samples (approximately 400 mg) that we had heated at 500 °C for 3 h and procedural reagent blanks were processed in parallel as controls. In addition, our study sample included 7.4 kg of Antarctic ice collected from the Graves Nunatak region in 2006 under GRA 06101.

Chemicals and Reagents

Sample-handling tools, ceramics, and glassware used for this study were rinsed with water, wrapped in aluminum foil, and heated in air at 500 °C overnight to remove any organic residue. Most of the chemicals used were purchased from Fisher Scientific, Sigma-Aldrich, or Acros Organics. Details of the sources of specific five-carbon (C₅) amino acids used as standards are available elsewhere (Glavin and Dworkin 2009). To prepare standard solutions for LC-FD/ToF-MS analysis, we dissolved individual compounds (97–99% pure) in Milli Q water and then combined them to enable their measurement in a single chromatographic separation. Solutions of sodium borate were prepared from solid sodium tetraborate decahydrate (Sigma Ultra 99.5–100% purity) that we baked in air at 500 °C for 3 h. All other solutions were prepared as previously described (Glavin et al. 2006).

Extraction Procedures and Analytical Techniques

The meteorite fragments were crushed into powders using a clean (see below) mortar and pestle in a laminar flow hood (Labconco, Kansas City, MO) under HEPA-filtered positive pressure. The ice sample was melted at room temperature in a 10 L plastic bucket that had been rinsed in Milli Q water, the ice meltwater was filtered with a 0.2 µm polyethylene membrane filter to remove particulate matter, concentrated using a rotoevaporator, and the residue brought up in Millipore water to a volume of 1 mL. The meteorite extraction and acid-hydrolysis procedures were performed as described previously (Glavin et al. 2006) except that prepacked PolyPrep AG-50W cation exchange columns (BioRad) were used in place of self-packed cation exchange columns. We immediately analyzed the *o*-phthaldialdehyde/*N*-acetyl-L-cysteine (OPA/NAC) derivatized samples by ultra performance liquid chromatography with fluorescence detection and time-of-flight mass spectrometry (LC-FD/ToF-MS) using a Waters ACQUITY ultrahigh performance liquid chromatograph and Waters

ACQUITY fluorescence detector connected in series to a Waters LCT Premier ToF-MS. Our chromatographic conditions and the positive electrospray and mass spectrometer conditions have been described in detail elsewhere (Glavin et al. 2006, 2010a). We identified amino acids in the meteorite and control samples by correlating sample peaks with known standards using both detected masses and chromatographic retention times, as detected by fluorescence and mass spectrometry.

Compound Specific Carbon Isotopic Analysis

Both the nonhydrolyzed and hydrolyzed extracts of the 435 mg LAP 02206 fragment were combined with the resulting acid-hydrolyzed extract from a second 4.75 g of LAP 02206. The total volume was dried, reacted with acidified isopropanol and trifluoroacetic anhydride to form volatile derivatives, and analyzed via gas chromatography coupled with mass spectrometry and isotope ratio mass spectrometry (GC-MS/IRMS) as described previously (Elsila et al. 2011), with few chromatographic conditions optimized for the separation of *n*- ω -amino acids. A 5 m base-deactivated fused silica guard column (Restek, 0.25 mm i.d.) and four 25 m Chirasil L-Val columns (Varian, 0.25 mm i.d.) were connected with Press-Tight connectors (Restek). The helium flow rate was 1.5 mL per minute and the following temperature program was used: initial oven temperature 50 °C, ramped at 10 °C min⁻¹ to 120 °C, ramped at 4 °C min⁻¹ to 175 °C, and held for 20 min.

RESULTS AND DISCUSSION

Meteoritic Amino Acids

Using LC-FD/ToF-MS, we determined the abundances of the two- to five-carbon (C₂ to C₅) acyclic, aliphatic, primary amino acids as well as ϵ -amino-*n*-caproic acid in thirteen different Antarctic meteorites including five Antarctic ureilites: ALHA77257, EET 83309 (a polymict ureilite), LEW 85328, GRA 95205, LAR 04315 (an anomalous ureilite); five Antarctic CV3 carbonaceous chondrites: ALH 84028, EET 96026, LAP 02206, GRA 06101, and LAR 06317; and three Antarctic CO3 carbonaceous chondrites: ALHA77307, MIL 05013, and DOM 08006. We also analyzed an interior fragment of Allende, thought to be more pristine than previously analyzed samples of this meteorite. The amino acids were extracted with hot water; half of the extracted sample was acid-vapor hydrolyzed to allow a comparison of the amino acids that contain primary amines following hot water extraction (“free amino acids”) with the total primary amino acids (free + bound) including those that can be converted to primary amines from

bound precursors (e.g., primary amide-containing carboxylic acids or aminonitriles). Representative chromatograms of acid-hydrolyzed hot water extracts are given in Fig. 1. The five ureilites had total amino acid concentrations ranging from 1000 to 2100 parts-per-billion (ppb), while the CV3 and CO3 chondrites showed a greater variability in total amino acid concentrations, with values ranging from 700 to 3200 ppb and from 260 to 2400 ppb, respectively (summarized in Table 1, abundance data for specific amino acids are available in Tables 2, 3, and 4). These values are greater than the total amino acid abundances found in the Almahata Sitta ureilite, and are 1–3 orders of magnitude lower than amino acid abundances previously measured in all but the most aqueously altered CI, CM, and CR carbonaceous chondrites (Glavin et al. 2010a).

We also determined the amino acid composition of a sample of blue ice collected from the Northern Graves Nunataks region of Antarctica (GRA ice 06-05; Table 3) as a control. This block of ice was sampled from the same location where the CV3 carbonaceous chondrite GRA 06101 was recovered. The total amino acid concentration of the Antarctic ice (less than one part per trillion, ppt) was 100,000-fold lower than the amino acid abundances measured in the Antarctic meteorites, including GRA 06101. In addition, the relative distributions of these amino acids are very different in the ice than in the meteorites. This is in contrast to previous analyses of Antarctic meteorites ALH 84001 and MacAlpine Hills 88105 (MAC 88105), where ice samples had similar amino acid distributions as the meteorites, leading to the conclusion that those amino acids came primarily from the ice (Bada et al. 1998). Although the overall amino acid distributions in the meteorites were distinct from the Antarctic ice, based on the low D/L ratios of the proteinogenic amino acids aspartic acid, glutamic acid, serine, alanine, and valine in many of the meteorites, they appear to have experienced varying degrees of terrestrial L-amino acid contamination after their fall to Earth. The total abundances of these protein amino acids are extremely low, making it difficult to assess what portions of these amino acids, if any, are indigenous to the meteorites. However, for ten of the fourteen meteorites in this study, chiral proteinogenic amino acids make up from 2% to 17% of the total amino acids, and surpass 40% of the total identified amino acids only in Allende and GRA 06101. The low overall abundances of the chiral proteinogenic amino acids in the Antarctic meteorites relative to nonproteinogenic amino acids indicate that amino acids of terrestrial origin contribute only a relatively small fraction of the total amino acids in these Antarctic meteorites.

In contrast to the proteinogenic amino acids, four nonproteinogenic amino acids, β -alanine (β -Ala),

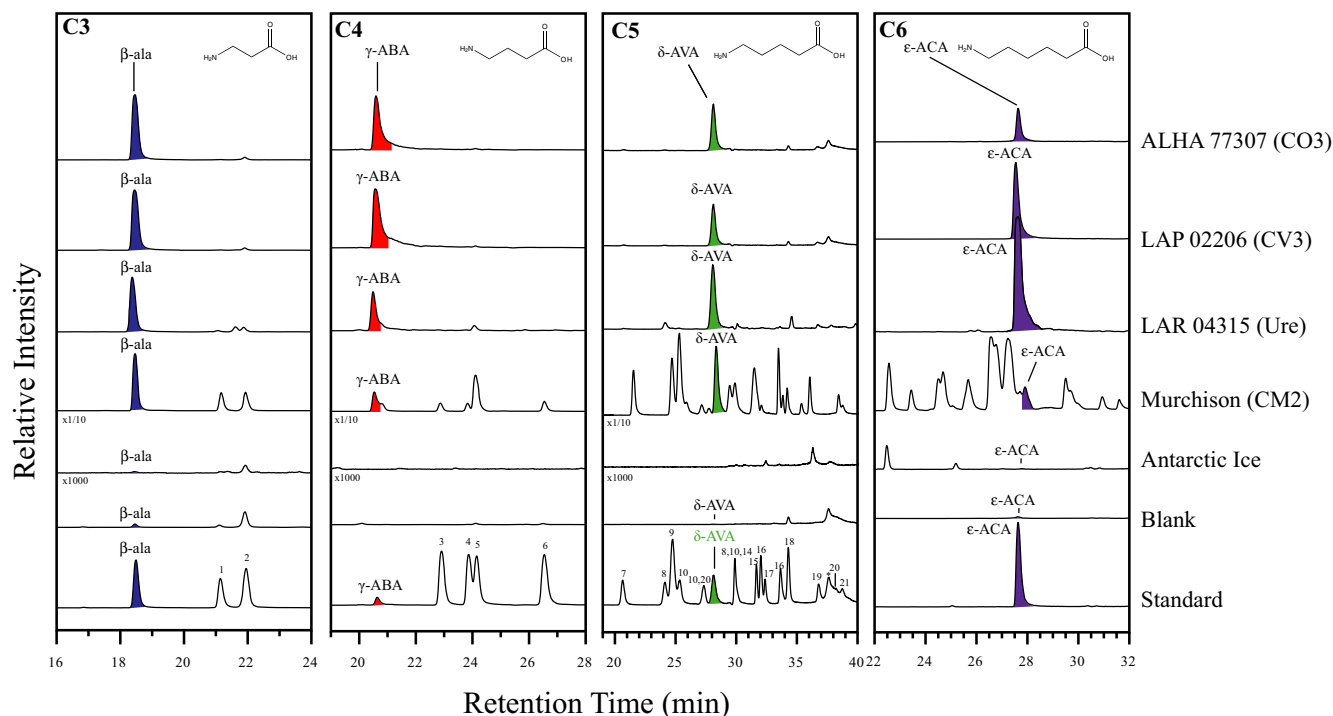


Fig. 1. Representative LC-ToF-MS single ion chromatograms of acid-hydrolyzed Antarctic meteorite samples, partial amino acid standards, and procedural blanks analyzed in this study. Chromatograms shown are for the C₃, C₄, and C₅, and C₆-carbon primary, aliphatic, acyclic amino acids (derivatized positive ionization mass-to-charge ratios of 351.1015, 365.1171, 379.1328, and 393.1485, respectively). The masses plotted represent a 0.07 Da window (the peak width at half maximum) centered around the corresponding theoretical monoisotopic masses of the mono-protonated positive ions of C₃ to C₅ OPA/NAC amino acid derivatives and are all set to the same scale. Traces obtained previously for Murchison, an aqueous altered CM2 carbonaceous chondrite, have been included for comparison. The traces have been set to the same scale to each other to facilitate comparison, except for the Murchison traces that have been reduced by a factor of ten. Peak numbers correspond to amino acid assignments in Table 2; the “*” denotes a contaminant with a mass similar to the C₅ aliphatic amino acids. Similar chromatograms were obtained for the remaining meteorites for both the hydrolyzed and nonhydrolyzed fractions.

γ -amino-*n*-butyric acid (γ -ABA), δ -amino-*n*-valeric acid (δ -AVA), and ϵ -amino-*n*-caproic acid (ϵ -ACA) are present in high abundance (comprise greater than 50% of the total measured amino acids) in thirteen of the fourteen meteorites analyzed in this study (Table 1). These four amino acids vary significantly in their free-to-bound ratios, ranging from 8% to >99% free (containing free amino groups without hydrolysis). High relative concentrations of free amino acids are a strong indicator of an extraterrestrial origin for those molecules. One of these amino acids, ϵ -ACA, is a monomer of Nylon-6 that has been shown to be a common contaminant introduced during sample curation of some meteorites and extraterrestrial samples (Glavin et al. 2006, 2010a; Elsila et al. 2009). However, ϵ -ACA derived from Nylon-6 exists overwhelmingly in the bound form because even its activated monomer is present as a lactam: the ϵ -ACA extracted from nylon sample bags for storing Antarctic meteorites and in shipping vials of Stardust mission aerogel samples was >99% bound

(Glavin et al. 2006, 2008). The meteorites, in contrast, have from 6% to 100% of their ϵ -ACA in free form (0–94% bound), providing a strong argument against the nylon bags as the source of ϵ -ACA in the meteorites. In addition, the variations in free versus bound compositions for the total *n*- ω -amino acid compositions (8–100% free; Table 1) further support their extraterrestrial origin—were the β -ala, γ -ABA, and δ -AVA, and ϵ -ACA to have come from a terrestrial source that the meteorites were all exposed to, such as the Antarctic ice, or during curation and processing, one would expect the percentage of free amino acids to be roughly the same in all of the samples. Most importantly, we were not able to detect any β -ala, γ -ABA, δ -AVA, or ϵ -ACA above the 0.01 ppb level in the Antarctic ice (Table 4). Therefore, we conclude that a large fraction of the nonprotein amino acids β -ala, γ -ABA, δ -AVA, and ϵ -ACA in these Antarctic meteorites are not derived from terrestrial contamination and are indigenous to the meteorites.

Table 1. Amino acid abundance data for the Antarctic ice, ureilite, and CV and CO meteorites.

Sample	Total identified amino acid abundances ^a	Total <i>n</i> - ω -amino acid abundances ^b	% of ϵ -ACA in free form ^c	% <i>n</i> - ω -amino acids in free form ^c
GRA Ice 06-05	0.2 pptr	< 0.03 pptr	nd	nd
Ureilites				
ALHA77257	2076 \pm 31	1807 \pm 28	> 99 ^d	86
EET 83309	1839 \pm 138	1730 \pm 138	9	23
LEW 85328	2112 \pm 268	2003 \pm 268	31	39
GRA 95205	2141 \pm 98	2106 \pm 98	21	28
LAR 04315	1598 \pm 251	1521 \pm 251	28	34
CV3 carbonaceous chondrites				
Allende	6137 \pm 509	482 \pm 25	17	70
ALH 84028	969 \pm 262	922 \pm 262	21	20
EET 96026	3193 \pm 398	3084 \pm 398	29	31
LAP 02206	3111 \pm 498	3037 \pm 497	27	32
LAR 06317	704 \pm 92	625 \pm 92	27	35
GRA 06101	863 \pm 272	262 \pm 68	23	27
CO3 carbonaceous chondrites				
ALHA77307	2428 \pm 315	2383 \pm 315	6	9
MIL 05013	261 \pm 34	210 \pm 34	6	8
DOM 08006	776 \pm 214	714 \pm 213	26	24

Note: nd = not determined.

^aAmino acid abundances given are given in parts-per-billion for the meteorites (ppb) and parts-per-trillion for the Antarctic ice, and were obtained for the amino acids listed in Tables 2–4.

^bTotals for *n*- ω -amino acids are defined as the sum of the part-per-billion abundances of β -Ala, γ -ABA, δ -AVA, and ϵ -ACA in the acid-hydrolyzed fraction for each meteorite.

^cThe free amino acid percentages for ϵ -ACA and the total *n*- ω -amino acids were calculated by dividing the respective abundances present in the nonhydrolyzed fraction by the abundances present in the hydrolyzed fractions.

^dValues of >99% are given where the abundances in the nonhydrolyzed fractions are greater than in the hydrolyzed fraction, indicating destruction of some amino acids during hydrolysis.

Predominance of *n*- ω -Amino Acids

We observed a compelling trend in the amino acid distributions of these thermally altered meteorites. The vast majority are straight chain amino acids in which the amino group is on the carbon farthest from the carboxylic acid (hereafter referred to as *n*- ω -amino acids). In eleven of the fourteen meteorites analyzed in this study, 72–99% of the three- to five-carbon primary aliphatic amino acids are *n*- ω -amino acids (β -ala, γ -ABA δ -AVA; structures shown in Fig. 1, data shown in Fig. 2). We have not included the two-carbon and six-carbon *n*- ω -amino acids (glycine and ϵ -aminocaproic [ϵ -ACA], respectively) in these totals because glycine has no amino acid isomers, and despite the clear predominance (Fig. 1) of ϵ -ACA among the six-carbon amino acids, the full suite of the six-carbon amino acids is not available commercially, preventing us from accurately quantifying the total abundance of the six-carbon amino acids. The relative abundances of *n*- ω -amino acids measured in these meteorites are notably higher than those previously observed in other carbonaceous meteorites. The next closest such isomer distribution is found in the aqueously altered CII carbonaceous chondrite Orgueil, at approximately 56% *n*- ω -amino acids, and most low temperature aqueously

altered carbonaceous chondrites are much lower, such as Murchison (CM2) at approximately 14% and QUE 99177 (CR2) at approximately 7% *n*- ω -amino acids (Glavin et al. 2010a).

Three of the analyzed meteorites, Allende, GRA 06101, and MIL 05013, also contain *n*- ω -amino acids, but they are a much smaller fraction of the total amino acids identified. A previous analysis of Allende revealed that at least one of its fragments was contaminated with L-proteinogenic amino acids (Botta et al. 2002), and our data on a different fragment of Allende also show elevated levels of L-enantiomers of aspartic acid, glutamic acid, alanine, and valine (Table 4). The large increases in the abundances of these amino acids during acid hydrolysis are consistent with their release from proteinogenic sources. For other amino acids, such as glycine, β -ala, and γ -ABA, the bulk of these compounds are present in the unhydrolyzed fraction in a free form, suggesting that they are indigenous to the meteorite. A closer look at the unhydrolyzed fraction of Allende reveals a lack of overall structural diversity among the four-carbon and five-carbon amino acids similar to the other thermally altered meteorites, excluding L-valine. Noticeably missing in Allende are several α -amino acids that are commonly found in aqueously altered meteorites such as α -aminoisobutyric acid (AIB), isovaline, and

Table 2. Summary of the average blank-corrected amino acid concentrations in unhydrolyzed (free) and acid-hydrolyzed (total) hot water extracts of Antarctic ureilites.^a Numbers after amino acid names refer to peaks shown in Fig. 1.

Amino acid	ALHA77257 (U)			EET 83309 (U)			LEW 83328 (U)			GRA 95205 (U)			LAR 04315 (U)		
	Free	Total		Free	Total		Free	Total		Free	Total		Free	Total	
D-aspartic	<0.1	<0.7		<0.2	<1.6		<0.1	<1.1		<0.8	<1.5		<0.8	<1.3	
L-aspartic	<1	<17		<1.9	<4.1		<1	<1.4		<2.8	<4.1		<2.1	<3.3	
L-glutamic	<1	18		0.8 ± 0.2	<0.3		1.2 ± 0.9	11.8 ± 1.3		4.5 ± 2.4	23 ± 5.9		1.2 ± 0.7	12.3 ± 2.9	
D-glutamic	<0.1	<5		<0.1	<0.1		0.3 ± 0.2	16.4 ± 5.4		0.2 ± 0.1	18 ± 3.4		<0.3	12.3 ± 3.6	
D-serine	<0.1	<0.1		1.8 ± 0.3	<0.3		1.1 ± 0.2	0.6 ± 0.1		<0.2	<0.3		<0.1	<0.1	
L-serine	6.1 ± 0.3	125 ± 7		5.7 ± 0.7	1.2 ± 0.9		5.2 ± 0.5	3.5 ± 1.6		7.8 ± 0.6	5.9 ± 0.6		4.5 ± 0.3	1.3 ± 0.4	
glycine	11 ± 1	80 ± 10		22 ± 1	7.4 ± 2.4		11 ± 2	63 ± 3		12 ± 2	36 ± 2		25 ± 3	24 ± 1	
ε-ACA	1403 ± 46	1368 ± 23		97 ± 9	1060 ± 130		295 ± 52	960 ± 227		280 ± 12	1317 ± 70		196 ± 24	710 ± 234	
C₃ amino acids															
β-alanine	43 ± 3	103 ± 4		76 ± 9	91 ± 11		60 ± 8	158 ± 14		81 ± 11	161 ± 13		63 ± 7	102 ± 6	
D-alanine, 1	4.6 ± 3.4	0.6 ± 0.4		3.9 ± 0.9	0.2 ± 0.1		<0.1	2.5 ± 0.3		1.3 ± 0.2	2.9 ± 0.5		1.7 ± 0.5	0.6 ± 0.2	
L-alanine, 2	42 ± 3.2	53 ± 5		2.2 ± 1.1	0.6 ± 0.1		4.6 ± 2.6	3.0 ± 0.7		3.6 ± 0.5	6.8 ± 1		1.1 ± 0.3	6.7 ± 0.9	
C₄ amino acids															
γ-aminobutyric	116 ± 21	285 ± 25		208 ± 22	575 ± 53		407 ± 160	815 ± 142		211 ± 20	561 ± 68		245 ± 31	558 ± 91	
D-β-aminobutyric, 3	4.1 ± 0.1	2.7 ± 0.2		2.1 ± 0.7	0.3 ± 0.1		0.2 ± 0.1	0.6 ± 0.2		1.2 ± 0.2	1.3 ± 0.2		<0.4	0.3 ± 0.1	
L-β-aminobutyric, 4	2.9 ± 0.7	3.4 ± 0.1		2.1 ± 0.5	0.4 ± 0.2		0.3 ± 0.1	0.5 ± 0.2		1.0 ± 0.1	1.2 ± 0.1		0.3 ± 0.2	0.2 ± 0.1	
α-aminobutyric, 5	0.7 ± 0.2	1.0 ± 0.1		0.2 ± 0.1	0.3 ± 0.1		0.8 ± 0.4	0.2 ± 0.1		1.4 ± 0.2	0.2 ± 0.1		0.5 ± 0.1	<0.1	
D,L-β-aminobutyric	<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1	
D,L-α-aminobutyric ^b , 6	<0.2	<0.1		<0.2	<0.2		<0.1	0.4 ± 0.2		<0.1	0.5 ± 0.3		0.2 ± 0.1	0.4 ± 0.2	
C₅ amino acids															
δ-aminovaleric	8.6 ± 1.6	51 ± 1		13 ± 3	4.4 ± 0.3		24 ± 3	71 ± 1		<12	66 ± 6		21 ± 0.4	151 ± 2	
3-aminobutyric, 7	0.5 ± 0.3	3.1 ± 0.6		<0.5	<0.1		<0.1	0.1 ± 0.1		<0.1	0.6 ± 0.2		<0.3	0.7 ± 0.4	
D,L-4-aminobutyric, 8	<0.1	0.2 ± 0.1		<0.2	<0.1		<0.1	1.5 ± 0.2		<0.5	<0.8		<0.2	8.7 ± 0.7	
D,L-4-aminobutyric, 9	<0.1	0.3 ± 0.1		<0.1	<0.1		<0.1	0.9 ± 0.8		<0.4	1.4 ± 0.2		<0.5	<0.1	
D,L-3-aminobutyric ^c , 10	0.4 ± 0.2	2.1 ± 0.2		<0.1	<0.1		<0.1	<0.1		<0.1	0.8 ± 0.3		<0.1	<0.1	
D,L-3-aminobutyric ^c , 11	<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1	
D,L-4-aminobutyric, 14	0.5 ± 0.3	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1	
D,L-3-aminobutyric ^c , 16	<0.1	3.6 ± 1.7		<0.2	<0.9		<0.4	<0.1		<0.1	<0.1		<0.1	1.3 ± 1.0	
L-isovaline, 17	<0.1	<0.3		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1	
L-valine, 18	3.7 ± 2.5	29 ± 1		4.7 ± 0.3	91 ± 1		4.8 ± 0.6	0.6 ± 0.1		3.5 ± 0.5	<0.1		3.5 ± 0.2	3.3 ± 1.5	
D-valine, 19	<0.1	2.7 ± 1.6		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1	
D-norvaline, 20	<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1	
L-norvaline, 21	<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1	
C ₃ -C ₆ n-oxo-amino acids ^d	1549 ± 48	1807 ± 28		393 ± 25	1730 ± 138		786 ± 166	2003 ± 268		584 ± 26	2106 ± 98		524 ± 40	1521 ± 251	
Total identified amino acids	1618 ± 49	2076 ± 31		443 ± 26	1839 ± 138		817 ± 167	2112 ± 268		613 ± 26	2141 ± 98		567 ± 40	1598 ± 251	

^aValues are reported in parts-per-billion (ppb) based on the bulk sample mass. Meteorite extracts were analyzed by OPA/NAC derivatization (1 and 15 min) and LC-FD/ToF-MS detection. Monoisotopic chromatograms were used for quantification of ToF-MS data and final peak integrations were background-corrected using a procedural blank. Peak areas in the sample chromatograms were compared with pure amino acid standards that were analyzed on the same day. Final values were normalized using desalting and derivatization recoveries based on the D,L-norleucine internal standard (recoveries were typically 70–80% for the meteorite extracts). Uncertainties (δ_x) were calculated from the standard error based on the number of separate measurements (n), $\delta_x = \sigma_x (n-1)^{-1/2}$. For all UV fluorescence data, coeluting peaks and/or compounds with interfering peaks were not included in the average. Upper limits are presented for amino acids that were not present at levels above the procedural blank background levels.

^bEnantiomers could not be separated under the chromatographic conditions.

^cEnantiomers could be separated, but not identified, due to a lack of optically pure standards.

^dThe total of the C₃-C₆ n-oxo-amino acids is defined as β-ala + γ-ABA + δ-AVA + ε-ACA.

Table 3. Summary of the average blank-corrected amino acid concentrations in unhydrolyzed (free) and acid-hydrolyzed (total) hot water extracts of Antarctic CV3 meteorites and Allende, a CV3 chondrite from Mexico.^a

Amino acid	ALH 84028			EET 96026			LAP 02206			LAR 06317			GRA 06101			Allende		
	Free	Total		Free	Total		Free	Total		Free	Total		Free	Total		Free	Total	
D-aspartic	0.2 ± 0.1	<1		0.2 ± 0.1	1.4 ± 0.8		<0.5	<2.7		1.3 ± 0.8	<1.2		<0.4	<2.1		<38	454 ± 47	
L-aspartic	0.8 ± 0.7	<2.6		1.1 ± 0.1	6.9 ± 3.5		<1.3	<0.9		4.6 ± 0.1	<1.5		<5.3	18 ± 3		<190	801 ± 233	
L-glutamic	1.4 ± 0.7	5.8 ± 1.7		1.1 ± 0.2	17 ± 2.4		<0.9	4.4 ± 1.5		2.6 ± 0.2	0.4 ± 0.3		0.5 ± 0.1	16 ± 4		49 ± 3	846 ± 412	
D-glutamic	0.3 ± 0.2	1.4 ± 0.9		0.3 ± 0.1	5.5 ± 0.7		<0.1	5.2 ± 0.5		0.2 ± 0.1	0.9 ± 0.2		<0.1	<2		29 ± 1	587 ± 128	
D-serine	<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	0.2 ± 0.1		0.5 ± 0.1	<0.1		47 ± 3	120 ± 19	
L-serine	0.4 ± 0.1	2.1 ± 1.1		3.0 ± 1.1	2.7 ± 0.2		2.7 ± 0.8	14.7 ± 0.3		5.0 ± 0.6	7.3 ± 3.9		9.9 ± 6.9	29 ± 5		206 ± 10	654 ± 67	
glycine	29 ± 1	19 ± 4		29 ± 1	57 ± 7		56 ± 2	120 ± 16		155 ± 12	49 ± 5		2.9 ± 0.8	47 ± 1		662 ± 52	851 ± 87	
ε-ACA	128 ± 18	611 ± 262		552 ± 31	1880 ± 338		426 ± 11	1560 ± 429		70 ± 2	315 ± 81		48 ± 9	211 ± 68		8.4 ± 1	50 ± 9	
C₃ amino acids																		
β-alanine	29 ± 1	112 ± 7		37 ± 3	144 ± 8		98 ± 5	271 ± 32		160 ± 20	181 ± 17		6.1 ± 0.2	5.0 ± 2.7		259 ± 14	295 ± 23	
D-alanine	0.5 ± 0.1	2.7 ± 1.0		0.2 ± 0.1	4.0 ± 1.6		0.7 ± 0.1	4.0 ± 0.9		0.8 ± 0.4	5.2 ± 2.1		0.9 ± 0.1	5.5 ± 3.3		54 ± 5	221 ± 12	
L-alanine	0.7 ± 0.1	6.7 ± 1.1		20 ± 3	7.5 ± 0.5		15 ± 1	8.0 ± 1.0		51 ± 4	10 ± 1		7.1 ± 3.0	275 ± 63		157 ± 9	686 ± 52	
C₄ amino acids																		
γ-aminobutyric	25 ± 1	158 ± 5		342 ± 13	979 ± 211		435 ± 39	1110 ± 250		27 ± 2	229 ± 72		16 ± 1	41 ± 2		49 ± 3	104 ± 6	
D-β-alanine	<0.1	<0.1		0.2 ± 0.1	0.2 ± 0.1		0.2 ± 0.1	0.2 ± 0.1		0.3 ± 0.1	<0.1		0.3 ± 0.1	0.3 ± 0.1		11 ± 10	6.6 ± 1.8	
L-β-alanine	<0.1	0.3 ± 0.2		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		0.3 ± 0.1	0.3 ± 0.1		1.5 ± 0.3	5.1 ± 2.0	
α-aminobutyric	0.2 ± 0.1	1.7 ± 1.0		0.3 ± 0.1	0.5 ± 0.1		0.5 ± 0.2	<0.1		0.2 ± 0.1	0.4 ± 0.1		0.5 ± 0.1	0.7 ± 0.1		<0.2	6.4 ± 1.6	
D,L-β-alanine	6.2 ± 1.1	14 ± 1		Trace	Trace		Trace	Trace		Trace	Trace		Trace	Trace		<0.1	<0.1	
D,L-α-aminobutyric ^b	<0.1	0.7 ± 0.5		0.2 ± 0.1	0.4 ± 0.3		<0.1	0.3 ± 0.1		<0.1	<0.1		<0.4	0.4 ± 0.1		2.4 ± 0.1	1.5 ± 3	
C₅ amino acids																		
δ-aminovaleric	4.6 ± 0.1	41 ± 11		11 ± 1	77 ± 5		18 ± 2	93 ± 1		<1.6	7.9 ± 0.4		1.6 ± 0.4	5.0 ± 1.1		20 ± 1	33 ± 1	
3-aminopentanoic	<0.1	<0.2		<0.1	1.4 ± 0.7		<0.1	<0.6		<0.1	<0.1		<0.1	<0.1		<0.2	1.0 ± 1	
D,L-4-aminopentanoic	<0.1	0.3 ± 0.2		<0.1	0.8 ± 0.3		<0.1	0.9 ± 0.2		<0.4	<0.1		<0.1	<0.1		<1.1	<0.8	
D,L-4-aminobutyric	<0.1	<0.1		<0.1	<0.1		<0.1	1.0 ± 0.9		<0.1	<0.1		<0.1	<0.1		<0.1	0.4 ± 0.1	
D,L-3-aminobutyric ^c	<0.1	<0.1		<0.1	<0.1		<0.1	0.3 ± 0.1		<0.3	<0.1		<0.1	<0.1		<0.1	<0.1	
D,L-3-aminopentanoic ^c	<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1	
D,L-4-aminobutyric	<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1	
D,L-4-aminopentanoic ^c	<0.1	<0.1		<0.1	<0.1		<0.1	1.8 ± 1.0		<0.1	<0.1		<0.1	<0.1		<0.1	0.5 ± 0.1	
L-isovaline	<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1	
L-valine	0.4 ± 0.2	2.0 ± 1.1		3.1 ± 1.7	2.4 ± 0.7		3.9 ± 2.0	5.2 ± 1.1		<1.8	2.1 ± 0.5		4.8 ± 2.1	5.8 ± 0.4		224 ± 15	370 ± 15	
D-valine	0.2 ± 0.1	0.2 ± 0.1		<0.1	0.9 ± 0.3		<0.1	1.8 ± 1.2		<0.1	<0.1		2.2 ± 1.3	3.1 ± 0.9		15 ± 1	30 ± 7	
D-norvaline	<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		0.5 ± 0.3	<0.1	
L-norvaline	<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		<0.1	<0.1		1.4 ± 0.1	1.3 ± 0.1	
C ₃ -C ₆ <i>n</i> -ω-amino acids ^d	186 ± 19	922 ± 262		942 ± 34	3084 ± 398		976 ± 41	3037 ± 497		259 ± 7	733 ± 110		72 ± 9	262 ± 68		336 ± 15	482 ± 25	
Total identified amino acids	194 ± 19	969 ± 262		986 ± 35	3193 ± 398		1038 ± 41	3111 ± 498		478 ± 15	801 ± 110		108 ± 12	863 ± 272		1829 ± 57	6137 ± 509	

^aValues are reported in parts-per-billion (ppb) based on the bulk sample mass, except for the ice values that are reported in parts-per-trillion (ppt). Meteorite extracts were analyzed by OPA/NAC derivatization (1 and 15 min) and LC-FD/ToF-MS detection. Monoisotopic chromatograms were used for quantification of ToF-MS data and final peak integrations were background-corrected using a procedural blank. Peak areas in the sample chromatograms were compared with pure amino acid standards that were analyzed on the same day. Final values were normalized using desalting and derivatization recoveries based on the D,L-norleucine internal standard (recoveries were typically 70–80% for the meteorite extracts). Uncertainties (δ_x) were calculated from the standard error based on the number of separate measurements (n), $\delta_x = \sigma_x (n-1)^{-1/2}$. For all UV fluorescence data, coeluting peaks and/or compounds with interfering peaks were not included in the average. Upper limits are presented for amino acids that were not present at levels above the procedural blank background levels.

^bEnantiomers could not be separated under the chromatographic conditions.

^cEnantiomers could be separated, but not identified, due to a lack of optically pure standards.

^dThe total of the C₃-C₆ *n*-ω-amino acids is defined as β-alanine + γ-ABA + ε-ACA. “Trace” denotes that a small amount of β-AIB could be observed, but because one its enantiomers co-elute with γ-ABA, its absolute abundance could not be determined.

Table 4. Summary of the average blank-corrected amino acid concentrations in unhydrolyzed (free) and acid-hydrolyzed (total) hot water extracts of the Antarctic CO3 meteorites and a sample of Antarctic ice from the northern Graves Nunataks region.^a

Amino acid	ALHA77307 (CO3)		MIL 05013 (CO3)		DOM 08006 (CO3)		GRA ice 06-05 (in pptr)	
	Free	Total	Free	Total	Free	Total	Free	Total
D-asp	1.1 ± 0.4	0.6 ± 0.4	0.4 ± 0.1	1.2 ± 0.1	1.0 ± 0.5	0.7 ± 0.6	0.01	0.01
L-asp	8.0 ± 1.1	2.0 ± 1.0	2.0 ± 1.1	1.6 ± 0.1	3.3 ± 1.4	0.6 ± 0.1	0.01	0.02
L-glu	8.9 ± 2.9	1.7 ± 0.1	1.9 ± 0.3	12 ± .3	0.9 ± 0.1	1.5 ± 0.9	<0.01	0.01
D-glu	0.2 ± 0.1	<0.1	0.2 ± 0.1	2.0 ± 0.6	<0.1	5.4 ± 1.4	<0.01	<0.01
D-ser	0.5 ± 0.2	<0.2	<0.1	<0.1	1.3 ± 0.5	1.1 ± 0.1	<0.01	<0.01
L-ser	36 ± 1	14 ± 1	2.1 ± 0.6	3.5 ± 1.4	7.1 ± 2.5	16 ± 2	0.02	0.05
gly	71 ± 5	7.5 ± 0.7	3.3 ± 0.4	13 ± 5	2.9 ± 1.7	19 ± 3	0.02	0.03
ε-ACA	73 ± 3	1290 ± 281	12 ± 2	190 ± 34	142 ± 65	550 ± 213	<0.01	<0.01
C ₃ amino acids								
β-ala	78 ± 2	279 ± 30	4.4 ± 0.5	13 ± 1	12 ± 1	58 ± 3	<0.01	<0.01
D-ala	1.7 ± 0.4	1.5 ± 0.4	0.9 ± 0.2	1.5 ± 0.4	1.4 ± 0.2	0.9 ± 0.4	0.01	0.01
L-ala	20 ± 5	9.5 ± 0.7	2.1 ± 0.1	2.5 ± 0.7	8.2 ± 1.1	5.5 ± 2.7	0.01	0.05
C ₄ amino acids								
γ-ABA	53 ± 4	781 ± 140	0.6 ± 0.2	5.0 ± 0.8	10 ± 1	81 ± 15	0.01	<0.01
D-β-ABA	0.7 ± 0.1	<0.1	<0.4	1.1 ± 0.2	0.5 ± 0.1	1.4 ± 0.2	<0.01	<0.01
L-β-ABA	<0.1	<0.1	0.4 ± 0.1	1.4 ± 0.5	<0.7	1.8 ± 0.2	<0.01	<0.01
α-AIB	0.9 ± 0.2	<0.3	0.6 ± 0.1	0.5 ± 0.1	<0.7	2.3 ± 1.1	<0.01	<0.01
D,L-β-AIB	Trace	Trace	9 ± 1.5	23 ± 3	4.6 ± 0.4	9.2 ± 1.3	<0.01	<0.01
DL-α-ABA ^b	<0.1	<0.2	<0.1	0.8 ± 0.4	0.6 ± 0.2	0.8 ± 0.2	<0.01	<0.01
C ₅ amino acids								
δ-AVA	4.5 ± 0.4	38 ± 2	0.4 ± 0.2	1.6 ± 0.9	3.4 ± 0.7	25 ± 4	<0.01	<0.01
3-a-2,2-dmpa	<0.1	<0.3	<0.1	0.3 ± 0.2	0.9 ± 0.1	0.3 ± 0.2	<0.01	<0.01
D,L-4-apa	<0.1	0.2 ± 0.1	0.2 ± 0.1	<0.2	<0.1	<0.1	<0.01	<0.01
D,L-4-a-3mba	<0.1	<0.2	<0.1	<0.1	<0.4	<0.1	<0.01	<0.01
D,L-3a-2-mba ^c	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.01	<0.01
D,L-3a-2-epa ^c	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.01	<0.01
D,L-4-a-2-mba	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.01	<0.01
D-iva	<0.1	<0.1	<0.1	<0.1	0.4 ± 0.2	1.5 ± 1.3	<0.01	<0.01
D,L-3-apa ^c	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.01	<0.01
L-iva	<0.1	<0.1	<0.1	<0.1	<0.1	0.5 ± 0.3	<0.03	<0.01
L-val	6.2 ± 1.5	6.0 ± 1.1	1.1 ± 0.4	4.6 ± 0.8	2.7 ± 0.1	2.1 ± 0.5	0.01	<0.01
D-val	<0.1	0.6 ± 0.4	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.4 ± 0.2	<0.01	<0.01
D-norval	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.01	<0.01
L-norval	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.01	<0.01
C ₃ -C ₆ <i>n</i> -ω-amino acids ^d	208 ± 5	2383 ± 315	17 ± 2	210 ± 34	168 ± 65	714 ± 213	<0.03	<0.03
Total identified amino acids	359 ± 11	2428 ± 315	42 ± 3	280 ± 34	201 ± 65	776 ± 214	0.1	0.2

^aValues are reported in parts-per-billion (ppb) based on the bulk sample mass. Meteorite extracts were analyzed by OPA/NAC derivatization (1 and 15 min) and LC-FD/ToF-MS detection. Monoisotopic chromatograms were used for quantification of ToF-MS data and final peak integrations were background-corrected using a procedural blank. Peak areas in the sample chromatograms were compared with pure amino acid standards that were analyzed on the same day. Final values were normalized using desalting and derivatization recoveries based on the D,L-norleucine internal standard (recoveries were typically 70–80% for the meteorite extracts). Uncertainties (δ_x) were calculated from the standard error based on the number of separate measurements (n), $\delta_x = \sigma_x (n-1)^{-1/2}$. For all UV fluorescence data, coeluting peaks and/or compounds with interfering peaks were not included in the average. Upper limits are presented for amino acids that were not present at levels above the procedural blank background levels.

^bEnantiomers could not be separated under the chromatographic conditions.

^cEnantiomers could be separated, but not identified, due to a lack of optically pure standards.

^dThe total of the C₃-C₆ *n*-ω-amino acids is defined as β-ala + γ-ABA + δ-AVA + ε-ACA.

norvaline (Glavin et al. 2010a). The remaining two meteorites, MIL 05013 (CO3; Table 4) and GRA 06101 (CV3; Table 3), also show a lack of diversity in their four-carbon and five-carbon amino acids. MIL 05013

does contain a significant fraction of *n*-ω-amino acids (60% of the three-carbon to five-carbon amino acids), although not as high as in the majority of the meteorites analyzed here. Due to its low overall amino acid

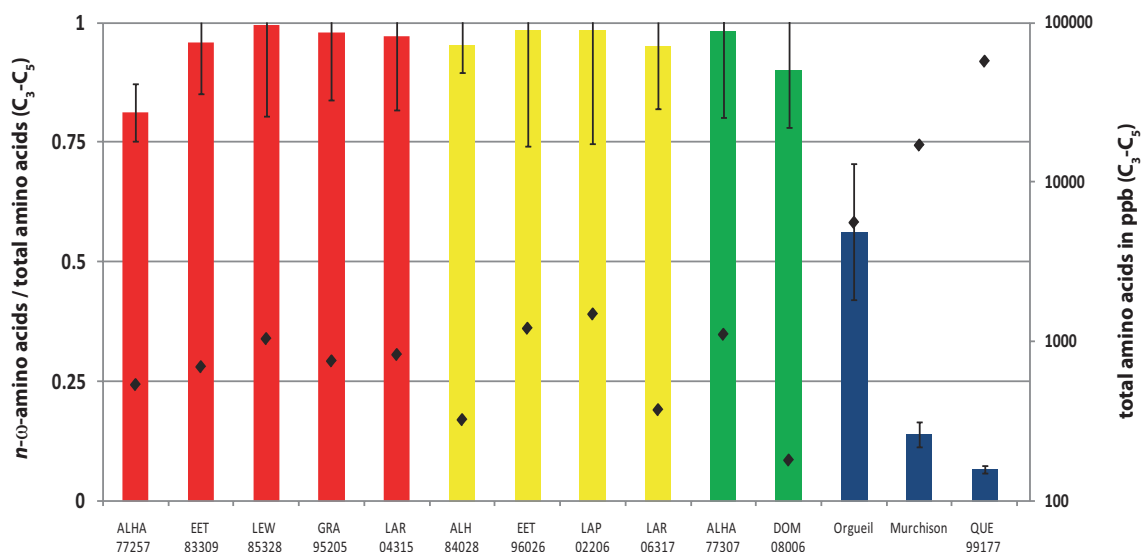


Fig. 2. Distribution and abundances of C₃ to C₅ amino acids in Antarctic meteorites. The primary axis shows the fraction of amino acids that are *n*- ω -isomers among thermally altered ureilite (red), CV3 carbonaceous chondrites (yellow), and CO3 carbonaceous chondrites (green). For comparison, the lower temperature aqueously altered meteorites Orgueil (CI1), Murchison (CM2), and QUE 99177 (CR3) have been included blue bars; taken from Glavin et al. (2010a). The secondary axis shows the total abundances of C₃ to C₅ amino acids in these meteorites (black diamonds, ppb). Errors bars were calculated using the standard errors given in Tables 2–4.

abundances, the presence of even a few ppb of terrestrial L-valine, for example, could appreciably reduce this value. In the case of GRA 06101, it could be argued that the L-alanine in excess of the D-alanine abundance is the result of terrestrial contamination, as it seems unlikely that such a large enantiomeric excess in a biological amino acid is indigenous to the meteorite, given that chiral α -H protein amino acids are prone to geologically rapid racemization under aqueous conditions at elevated temperatures (Bada 1972). If we assume a racemic mixture of 5.5 ppb each of indigenous D- and L-alanine, the fraction of *n*- ω -amino acids in GRA 06101 would be 70%, rather than the 14% calculated from the raw data. Thus, even the “outliers” in our study display some bias toward *n*- ω -amino acids, although the presence of terrestrial contaminants makes this less straightforward than for the other eleven more pristine meteorites shown in Fig. 2.

The predominance of *n*- ω -amino acids in ureilites and CV3 and CO3 carbonaceous chondrites is inconsistent with the generally accepted synthetic pathways for the formation of amino acids during aqueous alteration on the meteorite parent bodies. The amino acids in carbonaceous chondrites such as Orgueil, Murchison, and QUE 99177 were probably formed in postaccretion aqueous reactions such as the Strecker-cyanohydrin synthesis of α -amino acids or Michael addition of ammonia to unsaturated nitriles to make β -amino acids (Miller 1957; Peltzer et al. 1984; Ehrenfreund et al. 2001). While CV3 and CO3 carbonaceous chondrites do show

minor indications of aqueous alteration, its duration, and overall influence is minimal for most of these meteorites (Brearley 2006); ureilites show little evidence of low-temperature aqueous alteration (e.g., Almahata Sitta, Zolensky et al. 2010). Therefore, one or more different synthetic routes that are not dependent on low-temperature aqueous chemical reactions were likely responsible for the amino acid formation in these meteorites; this is consistent with the observation that many soluble organics in meteorites are isotopically inconsistent with the Strecker-type mechanisms. Most abiotic processes result in structural diversity, with little selectivity toward specific structural isomers in their product distributions. There are no generally accepted synthetic pathways that can explain the bias toward *n*- ω -amino acids observed in ureilites and CV3 and CO3 carbonaceous chondrites. However, the predominance of straight-chain isomers and the elevated temperatures the parent asteroids experienced are consistent with Fischer Tropsch-/Haber Bosch-type mineral-catalyzed synthesis reactions (hereafter referred to as FTT, or Fischer Tropsch-type) of N₂, H₂, and CO that have been implicated in a myriad of reactions in the solar system (Studier et al. 1968; Anders et al. 1973; Levy et al. 1973).

Modeling has suggested that temperatures and pressures present in the asteroid belt would be particularly well-suited for FTT reactions (Kress and Tielens 2001). In addition, previous studies have shown that gas phase reactions of CO, H₂, and NH₃ can produce a variety of amino acids (Yoshino et al. 1971), and there has been

considerable debate in the literature as to whether or not FTT reactions are responsible for the organic molecules observed in meteorites (Hayatsu and Anders 1981; Cronin and Pizzarello 1990; Kerridge 1999). However, amino acids produced by laboratory FTT reactions have only been compared with amino acid inventories observed in CM chondrites that probably resulted from aqueous Strecker reactions, not FTT reactions. The putative *n*- ω -amino acid signature of nebular FTT-reactions may have been lost in aqueously altered meteorites because aqueous parent-body processes produce much larger quantities of structurally diverse amino acids. Such amino acid “overprinting” from Strecker reactions may not have occurred in the thermally altered meteorites studied here because aqueous alteration was not the dominant process occurring in these meteorites. Quantitative comparisons of amino acid compositions between laboratory-produced FTT amino acids and those observed in the thermally altered meteorites reported here are needed to test if this mechanism is consistent with predominant *n*- ω -amino acid formation. If the FTT hypothesis is correct, these meteorites should also contain primarily *n*-alkanes and *n*-carboxylic acids. However, we found only one report on hydrocarbons in any of the Antarctic meteorites we studied, ALHA77307 (Murae et al. 1984), and no carboxylic acid analyses for these Antarctic meteorites have been published. The discovery of amino acids in these thermally altered meteorites will hopefully provide the impetus for such studies.

Carbon Isotopic Measurements

Carbon isotopic measurements of amino acids in thermally altered meteorites have not been reported previously. For the first time, we measured the compound-specific stable carbon isotopic ratio for γ -ABA and ϵ -ACA in the CV3 carbonaceous chondrite LAP 02206. Almost all of the ϵ -ACA detected in this meteorite is in the free form, indicating that it is not a result of terrestrial nylon contamination. The $\delta^{13}\text{C}$ values were $-27\text{‰} \pm 8\text{‰}$ for γ -ABA and $-23\text{‰} \pm 7\text{‰}$ for ϵ -ACA. We were unable to determine the isotopic composition for the other *n*- ω -amino acids due to anomalous, poor recoveries during extraction and work-up of the larger portion of LAP 02206. These carbon isotopic values are clearly distinct from the compound-specific values measured for amino acids in CM, CR, and CI meteorites, which typically range from $+5\text{‰}$ to $+50\text{‰}$ (Engel et al. 1990; Ehrenfreund et al. 2001; Pizzarello and Cooper 2001; Pizzarello et al. 2004; Martins et al. 2007). The lower $\delta^{13}\text{C}$ values observed in LAP 02206 are similar to those measured in biologically derived amino acids (e.g., Scott et al. 2006). However, as discussed above, the low abundances of chiral

proteinogenic amino acids and the relatively high abundances of nonproteinogenic amino acids in the free form are inconsistent with known sources of terrestrial contamination. Rather, we believe that the measured ^{13}C depletion is a signature of the formation process of these amino acids. In the aqueously altered meteorites that have previously been analyzed, enrichment in ^{13}C , ^{15}N , and ^2H in amino acids indicates a low-temperature, interstellar origin for the compounds or their precursors (Cronin and Chang 1993). FTT reactions occurring under different temperature and environmental conditions would probably produce a distinct isotopic signature. Laboratory investigations of hydrocarbons produced by FTT reactions under conditions relevant to the solar nebula have shown kinetic isotope effects producing saturated hydrocarbons that are isotopically lighter than the initial CO (Lancet and Anders 1970; Yuen et al. 1990; Hu et al. 1998). FTT reactions performed under hydrothermal conditions also produce hydrocarbons depleted in ^{13}C , with the total magnitude of carbon isotopic fractionation similar to that produced by many terrestrial biological processes (McCollom and Seewald 2006). Previous measurements of both meteoritic and fungal-produced amino acids also emphasized the importance of context and formation processes in interpreting carbon isotopic values as terrestrial or extraterrestrial (Elsila et al. 2011). Given these previous hydrocarbon measurements, it is likely that FTT-produced amino acids would also be depleted in ^{13}C , possibly to a $\delta^{13}\text{C}$ ratio similar to that produced by terrestrial biology. The $\delta^{13}\text{C}$ values we measured for γ -ABA and ϵ -ACA are consistent with this hypothesis. Further testing would require the analysis of carbon isotopic fractionation of amino acids produced by FTT reactions in the laboratory, as well as additional meteoritic samples. On the basis of abundances in the meteorites analyzed herein, and approximately 10^{-9} mol detection limits using state-of-the-art isotopic ratio measurements, we calculate that 1–10 g of each meteorite would be required to make carbon isotope measurements of the most abundant amino acids in these meteorites.

Timing of Amino Acid Formation in Thermally Altered Meteorites

Our observation of amino acids in five ureilites of monomict, polymict, and anomalous subtypes makes a strong argument that these molecules are widespread among thermally altered meteorites. It is improbable that the *n*- ω -amino acids observed in the ureilites were formed prior to the parent-body thermal alteration event because amino acids are susceptible to decarboxylation at high temperatures (Rodante 1992; Li and Brill 2003). Half-lives for gas-phase thermal decarboxylation reactions of amino and carboxylic

acids are on the order of 1–100 yr at 500 °C and just 1–500 ms at 1200 °C (extrapolated from Nguyen et al. 1995; (Li and Brill 2003)). Although ureilites experienced rapid cooling from >1000 to approximately 650 °C at a rate of approximately 10 °C per hour (Goodrich et al. 2001, 2004), just 10 min at 1200 °C is equivalent to over 100,000 half-lives; therefore, this temperature profile would have completely destroyed any preexisting amino acids. At 300 °C, a temperature that CV3 and CO3 carbonaceous chondrites probably experienced (Brearley 2006), carboxylic acid groups have gas-phase decarboxylation half-lives of 10^6 – 10^9 yr, durations that are more compatible with their survival. Thus, the surviving amino acids in thermally altered meteorites were unlikely to have formed before they were cooler than 500 °C (Rodante 1992; Glavin and Bada 2001). Temperatures below 500 °C are increasingly compatible with the FTT reactions mentioned above. Alternatively, it is possible that molecules synthesized in the solar nebula (Thaddeus 2006) such as H₂, H₂O, N₂, NH₃, CO, or more complex organic molecules became trapped in asteroid parent bodies during accretion. If the accretion process resulted in an essentially closed system, subsequent heating of the parent bodies during thermal alteration could serve to “recycle” the atoms, converting water to hydrogen and oxygen, amine-containing compounds to ammonia or nitrogen gas, carbonyls or alcohols to CO, and branched chain amino acids to their component parts. These simple molecules could then serve as feedstock for mineral-catalyzed FTT reactions, potentially leading to *n*- ω -amino acids.

CONCLUSION

The observation that amino acids, molecules essential for life as we know it, are formed in unexpected extraterrestrial environments reinforces the inevitability of chemical reactions in the universe. It is becoming increasingly clear that petrology, temperature, and the relative activity of water on a given asteroid have a significant impact on the chemical reactions that take place. The consequences of this “cosmochemical selection” are that the types and abundances of the molecules formed are generally consistent among meteorites of the same class and alteration history, while varying across classes with different alteration histories. In the case of CV3, CO3, and ureilite chemical syntheses, it appears that similar cosmochemical selection mechanisms existed to favor the formation/survival of *n*- ω -amino acids while aqueously altered carbonaceous chondrites experienced different selection conditions, as evidenced by the structural diversity of their amino acids and other organic molecules.

Acknowledgments—A. S. B. acknowledges support from the NASA Postdoctoral Program, administered by Oak

Ridge Associated Universities through a contract with NASA. The authors acknowledge funding support from the NASA Astrobiology Institute and the Goddard Center for Astrobiology and the NASA Cosmochemistry Program. We thank K. Righter (NASA Johnson Space Center) for providing the Antarctic meteorites and for helpful discussions; the 2006 ANSMET team for providing the Antarctic ice sample; G. Matrajt for providing the sample of Allende; and an anonymous reviewer and Z. Martins for helpful comments and criticisms of the manuscript.

Editorial Handling—Dr. Scott Sandford

REFERENCES

- Anders E., Hayatsu R., and Studier M. H. 1973. Organic compounds in meteorites. *Science* 182:781–790.
- Bada J. L. 1972. Kinetics of racemization of amino acids as a function of pH. *Journal of the American Chemical Society* 94:1371–1373.
- Bada J. L., Glavin D. P., McDonald G. D., and Becker L. 1998. A search for endogenous amino acids in Martian meteorite ALH 84001. *Science* 279:362–365.
- Botta O., Glavin D. P., Kminek G., and Bada J. L. 2002. Relative amino acid concentrations as a signature for parent body processes of carbonaceous chondrites. *Origins of Life and Evolution of the Biosphere* 32:143–163.
- Brearley A. J. 2006. The action of water. In *Meteorites and the early solar system II*, edited by Lauretta D. S. and McSween H. J. Jr. Tucson, AZ: The University of Arizona Press. pp. 584–624.
- Burton A. S., Glavin D. P., Callahan M. P., Dworkin J. P., Jenniskens P., and Shaddad M. H. 2011. Heterogeneous distributions of amino acids provide evidence of multiple sources within the Almahata Sitta parent body, asteroid 2008 TC₃. *Meteoritics & Planetary Science* 46:1703–1712.
- Chyba C. and Sagan C. 1992. Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules: An inventory for the origins of life. *Nature* 355:125–132.
- Cooper G., Kimmich N., Belisle W., Sarinana J., Brabham K., and Garrel L. 2001. Carbonaceous meteorites as a source of sugar-related organic compounds for the early Earth. *Nature* 414:879–883.
- Cronin J. R. and Chang S. 1993. Organic matter in meteorites: Molecular and isotopic analyses of the Murchison meteorite. In *The chemistry of life's origins*, edited by Greenberg J. M. Boston: Kluwer. pp. 209–258.
- Cronin J. R. and Moore C. B. 1971. Amino acid analyses of the Murchison, Murray, and Allende carbonaceous chondrites. *Science* 172:1327–1329.
- Cronin J. R. and Moore C. B. 1976. Amino acids of the Nogoya and Mokoia carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 40:853–857.
- Cronin J. R. and Pizzarello S. 1990. Aliphatic hydrocarbons of the Murchison meteorite. *Geochimica et Cosmochimica Acta* 54:2859–2868.
- Dodd R. T. 1981. *Meteorites, a petrologic-chemical synthesis*. New York: Cambridge University Press. 368. p.
- Ehrenfreund P., Glavin D. P., Botta O., Cooper G., and Bada J. L. 2001. Extraterrestrial amino acids in Orgueil and

- Ivuna: Tracing the parent body of CI type carbonaceous chondrites. *Proceedings of the National Academy of Sciences* 98:2138–2141.
- Elsila J. E., Glavin D. P., and Dworkin J. P. 2009. Cometary glycine detected in samples returned by Stardust. *Meteoritics & Planetary Science* 44:1323–1330.
- Elsila J. E., Callahan M. P., Glavin D. P., Dworkin J. P., and Brückner H. 2011. Distribution and stable isotopic composition of amino acids from fungal peptaibiotics: Assessing the potential for meteoritic contamination. *Astrobiology* 11:123–133.
- Engel M. H., Macko S. A., and Silfer J. A. 1990. Carbon isotope composition of individual amino acids in the Murchison meteorite. *Nature* 348:47–49.
- Glavin D. P. and Bada J. L. 2001. Survival of amino acids in micrometeorites during atmospheric entry. *Astrobiology* 1:259–269.
- Glavin D. P. and Dworkin J. P. 2009. Enrichment of the amino acid L-isovaline by aqueous alteration on CI and CM meteorite parent bodies. *Proceedings of the National Academy of Sciences* 106:5487–5492.
- Glavin D. P., Dworkin J. P., Aubrey A., Botta O., Doty J. H., Martins Z., and Bada J. L. 2006. Amino acid analyses of Antarctic CM2 meteorites using liquid chromatography-time of flight-mass spectrometry. *Meteoritics & Planetary Science* 41:889–902.
- Glavin D. P., Dworkin J. P., and Sandford S. A. 2008. Detection of cometary amines in samples returned by Stardust. *Meteoritics & Planetary Science* 43:399–413.
- Glavin D. P., Callahan M. P., Dworkin J. P., and Elsila J. E. 2010a. The effects of parent body processes on amino acids in carbonaceous chondrites. *Meteoritics & Planetary Science* 45:1948–1972.
- Glavin D. P., Aubrey A. D., Callahan M. P., Dworkin J. P., Elsila J. E., Parker E. T., Bada J. L., Jenniskens P., and Shaddad M. H. 2010b. Extraterrestrial amino acids in the Almahata Sitta meteorite. *Meteoritics & Planetary Science* 45:1695–1709.
- Goodrich C. A. 1999. Are ureilites residues from partial melting of chondritic material? The answer from MAGPOX. *Meteoritics & Planetary Science* 34:109–119.
- Goodrich C. A., Fioretti A. M., Tribaudino M., and Molin G. 2001. Primary trapped melt inclusions in olivine in the olivine-augite-orthopyroxene ureilite Hughes 009. *Geochimica et Cosmochimica Acta* 65:621–652.
- Goodrich C. A., Scott E. R. D., and Fioretti A. M. 2004. Ureilitic breccias: Clues to the petrologic structure and impact disruption of the ureilite parent asteroid. *Chemie der Erde—Geochemistry* 64:283–327.
- Hayatsu R. and Anders E. 1981. Organic compounds in meteorites and their origins. *Topics in Current Chemistry* 99:1–37.
- Herrin J. S., Zolensky M. E., Ito M., Le L., Mittlefehldt D. W., Jenniskens P., Ross A. J., and Shaddad M. H. 2010. Thermal and fragmentation history of ureilitic asteroids: Insights from the Almahata Sitta fall. *Meteoritics & Planetary Science* 45:1789–1803.
- Higuchi H., Morgan J. W., Ganapathy R., and Anders E. 1976. Chemical fractionations in meteorites—X Ureilites. *Geochimica et Cosmochimica Acta* 40:1563–1571.
- Hu G., Ouyang Z., Wang X., and Wen Q. 1998. Carbon isotopic fractionation in the process of Fischer-Tropsch reaction in primitive solar nebula. *Science in China Series D: Earth Sciences* 41:202–207.
- Huss G. R., Rubin A. E., and Grossman J. N. 2006. Thermal metamorphism in chondrites. In *Meteorites and the early solar system*, edited by Lauretta D. and McSween H. J. Tucson, AZ: The University of Arizona Press. pp. 567–586.
- Kerridge J. F. 1999. Formation and processing of organics in the early solar system. *Space Science Reviews* 90:275–288.
- King E. Jr., Schonfeld E., Richardson K., and Eldridge J. 1969. Meteorite fall at Pueblito de Allende, Chihuahua, Mexico: Preliminary information. *Science* 163:928–929.
- Kress M. E. and Tielens A. G. G. M. 2001. The role of Fischer-Tropsch catalysis in solar nebula chemistry. *Meteoritics & Planetary Science* 36:75–91.
- Krot A. N., Hutcheon I. D., Brearley A. J., Pravdivtseva O. V., Petaev M. I., and Hohenberg C. M. 2006. Timescales and settings for alteration of chondritic meteorites. In *Timescales and settings for alteration of chondritic meteorites, II*, edited by Lauretta D. and McSween H. J. Tucson, AZ: The University of Arizona Press. pp. 525–553.
- Kvenvolden K., Lawless J., Pering K., Peterson E., Flores J., Ponnamperna C., Kaplan I. R., and Moore C. 1970. Evidence for extraterrestrial amino-acids and hydrocarbons in the Murchison meteorite. *Nature* 228:923–926.
- Lancet M. S. and Anders E. 1970. Carbon isotope fractionation in the Fischer-Tropsch synthesis and in meteorites. *Science* 170:980–982.
- Levy R. L., Grayson M. A., and Wolf C. J. 1973. The organic analysis of the Murchison meteorite. *Geochimica et Cosmochimica Acta* 37:467–483.
- Li J. and Brill T. B. 2003. Decarboxylation mechanism of amino acids by density functional theory. *The Journal of Physical Chemistry A* 107:5993–5997.
- Martins Z., Alexander C. M. O., Orzechowska G. E., Fogel M. L., and Ehrenfreund P. 2007. Indigenous amino acids in primitive CR meteorites. *Meteoritics & Planetary Science* 42:2125–2136.
- McCormell T. M. and Seewald J. S. 2006. Carbon isotope composition of organic compounds produced by abiotic synthesis under hydrothermal conditions. *Earth and Planetary Science Letters* 243:74–84.
- Miller S. L. 1957. The mechanism of synthesis of amino acids by electric discharges. *Biochimica et Biophysica Acta* 23:480–489.
- Mittlefehldt D. W., McCoy T. J., Goodrich C. A., and Kracher A. 1998. Non-chondritic meteorites from asteroidal bodies. In *Planetary materials*, edited by Papike J. J. Washington, D.C.: Mineralogical Society of America. pp. 4–1–4–195.
- Murae T., Masuda A., and Takahashi T. 1984. Pyrolytic studies of organic components in Antarctic carbonaceous chondrites Y-74662 and ALH77307. *Memoirs of National Institute of Polar Research Special Issue* 35:250–256.
- Nguyen M. T., Sengupta D., Raspoet G., and Vanquickenborne L. G. 1995. Theoretical study of the thermal decomposition of acetic acid: Decarboxylation versus dehydration. *The Journal of Physical Chemistry* 99:11883–11888.
- Peltzer E. T., Bada J. L., Schlesinger G., and Miller S. L. 1984. The chemical conditions on the parent body of the Murchison meteorite: Some conclusions based on amino, hydroxy and dicarboxylic acids. *Advances in Space Research* 4:69–74.
- Pizzarello S. and Cooper G. W. 2001. Molecular and chiral analyses of some protein amino acid derivatives in the

- Murchison and Murray meteorites. *Meteoritics & Planetary Science* 36:897–909.
- Pizzarello S., Huang Y., and Fuller M. 2004. The carbon isotopic distribution of Murchison amino acids. *Geochimica et Cosmochimica Acta* 68:4963–4969.
- Rodante F. 1992. Thermodynamics and kinetics of decomposition processes for standard [alpha]-amino acids and some of their dipeptides in the solid state. *Thermochimica Acta* 200:47–61.
- Rubin A. E. 1988. Formation of ureilites by impact-melting of carbonaceous chondritic material. *Meteoritics* 23:333–337.
- Scott J. H., O'Brien D. M., Emerson D., Sun H., McDonald G. D., Salgado A., and Fogel M. L. 2006. An examination of the carbon isotope effects associated with amino acid biosynthesis. *Astrobiology* 6:867–880.
- Sephton M. A. 2002. Organic compounds in carbonaceous meteorites. *Natural Product Reports* 19:292–311.
- Studier M. H., Hayatsu R., and Anders E. 1968. Origin of organic matter in early solar system—I hydrocarbons. *Geochimica et Cosmochimica Acta* 32:151–173.
- Thaddeus P. 2006. The prebiotic molecules observed in the interstellar gas. *Philosophical Transactions of the Royal Society B: Biological Sciences* 361:1681–1687.
- Weisberg M., McCoy T., and Krot A. 2006. Systematics and evaluation of meteorite classification. In *Meteorites and the early solar system II*, 2nd ed., edited by Lauretta D. and McSween H. J. Tucson, AZ: The University of Arizona Press. pp. 19–52.
- Yoshino D., Hayatsu K., and Anders E. 1971. Origin of organic matter in early solar system—III. Amino acids: Catalytic synthesis. *Geochimica et Cosmochimica Acta* 35:927–938.
- Yuen G. U., Pecore J. A., Kerridge J. F., Pinnavaia T. J., Rightor E. G., Flores J., Wedeking K., Mariner R., Des Marais D. J., and Chang S. 1990. Carbon isotope fractionation in Fischer-Tropsch type reactions (abstract). 21st Lunar and Planetary Science Conference. pp. 1367–1368.
- Zolensky M., Herrin J., Mikouchi T., Ohsumi K., Friedrich J., Steele A., Rumble D., Fries M., Sandford S., Milam S., Hagiya K., Takeda H., Satake W., Kurihara T., Colbert M., Hanna R., Maisano J., Ketcham R., Goodrich C. A., Le L., Robinson G., Martinez J., Ross K., Jenniskens P., and Shaddad M. H. 2010. Mineralogy and petrography of the Almahata Sitta ureilite. *Meteoritics & Planetary Science* 45:1618–1637.
-